Hydrogenation of Canola Oil in the Presence of Nickel and the Methyl Benzoate-Chrome Carbonyl Complex

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Canola oil was hydrogenated using a mixture of homogeneous methyl benzoate-$Cr(CO)_3$ and heterogeneous nickel catalysts. The effect of the methyl benzoate-$Cr(CO)_3$-to-nickel ratio on the activity, specific isomerization index, linoleate and linolenate selectivities, and fatty acid composition was evaluated, and the results compared with those obtained with commercial nickel catalyst and methyl benzoate-$Cr(CO)_3$ used individually. At higher chromium-to-nickel ratios the activity of nickel was inhibited and the system behaved essentially like the pure chrome complex, while at low chromium-to-nickel ratios the characteristics of the nickel predominated. In a short transition zone relatively high reaction rates were obtained with significantly reduced *trans*-isomer levels in the product. In a broader sense, it may be possible to combine a homogeneous and heterogeneous catalyst while retaining the advantages of both. We may thus be able to design catalyst systems for specific applications.

Edible oils are industrially hydrogenated using heterogeneous nickel catalysts, which are very active; however, they also catalyze the *cis-trans* interconversion of double bonds and permit the migration of double bonds along the chain (1). In naturally occurring oils the double bonds are almost always in the *cis* configuration (2). Davignon et al. (3) have pointed out the need to develop new selective catalysts that conserve linoleic acid and minimize *trans*-isomer formation during hydrogenation of fats and oils. On the other hand, Applewhite (4) has reviewed the recent literature on the nutritional effects of hydrogenated soybean oil, and concluded that there were no adverse effects of *trans*-isomers as long as the diet contained a sufficient level of essential fatty acids. Also, the recent report by the Federation of American Societies for Experimental Biology (5) concluded there was no evidence in the literature demonstrating or suggesting reasonable grounds to suspect a hazard to public health when hydrogenated oils were used. Although an important consideration at the beginning of this project was to minimize the *trans* content during hydrogenation, the emphasis soon shifted to the development of new catalyst systems as such.

Our approach to selective hydrogenation of triglyceride oils has been the use of soluble organometallic compounds as catalysts. Frankel and his co-workers (6-9) reported that, in the homogeneous hydrogenation of soybean oil with arene-$Cr(CO)_3$ complexes, the polyunsaturated fatty acids were selectively hydrogenated, forming products in which the double bonds were predominantly in the *cis* configuration. Also, in a recent study (10) it was reported that $RuCl_2(CO)_2(PPH_3)_2$ is a very active catalyst with the potential for producing partially hydrogenated oils with reduced *trans*-isomer concentrations.

Rapeseed oil has been the source of edible oils in many parts of the world. In the last two decades Canadian plant breeders have developed new rapeseed cultivars which yield an oil low in erucic acid (0.3-1.7%) and a meal low in glucosinolates (about 20 μmoles/g). These cultivars were named "canola" by the Canadian rapeseed industry (11). Literature on the hydrogenation characteristics of canola is limited. However, in recent years a number of articles have been published by deMan and his co-workers (12-20), who examined the hydrogenation behavior of these oils with commercial heterogeneous nickel catalysts.

There are a few reports in the literature on the modification of the activity and selectivity of heterogeneous catalysts for edible-oil hydrogenation by introducing small amounts of another heterogeneous catalyst. In one of these reports, Moulton et al. (21) reported on the hydrogenation of soybean oil with mixed copper chromite and nickel catalysts to show the effect of small amounts of nickel on the hydrogenation rate and the composition of the partially hydrogenated oil. Their study indicated that small amounts of nickel enhanced the activity of copper chromite without greatly altering the character of the hydrogenated oil. A similar study was reported by Paterson (22), who investigated the hydrogenation of soybean oil using a nickel catalyst which contained small amounts of copper and chromium. This mixed catalyst had strong decolorizing properties in addition to its catalytic activity for hydrogenation.

In a recent article, Diosady et al. (23) reported on the hydrogenation of canola oil using methyl benzoate-$Cr(CO)_3$, benzene-$Cr(CO)_3$ and toluene-$Cr(CO)_3$ as homogeneous catalysts. The effect of temperature, pressure and catalyst concentration on the specific isomerization index, linolenate selectivity and hydrogenation activity was measured and compared with that of commercial nickel catalyst. The *trans* content of oils hydrogenated using methyl benzoate-chromium tricarbonyl as a catalyst was 6.5% at an iodine value of 90, which is significantly lower than the 20-30% obtained in comparable nickel runs. The resulting oil was high in monoenes and low in saturates and *trans*-isomer content.

Unfortunately, these chrome carbonyl catalysts are less active than nickel and are difficult to separate from the oil. The immobilization of these catalysts on a solid support may be a promising avenue for the development of highly selective catalysts (24-26). However, their activity must be significantly increased before they could gain commercial acceptance.

The main objective of this program is to investigate mixed-catalyst systems in which a heterogeneous catalyst is used in combination with a homogeneous

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catalyst. Such systems apparently have not been reported previously in the literature. In the present study the properties of a mixed catalyst consisting of methyl benzoate-$Cr(CO)_3$ and nickel are reported. This mixed catalyst may be expected to combine the *cis* selectivity of the chrome carbonyls with the high activity of nickel.

MATERIALS AND METHODS

Methyl benzoate-chromium tricarbonyl (20% Cr) was purchased from Strem Chemicals, Newburyport, Massachusetts. AOCS "standard nickel catalyst" containing 25% nickel was obtained from the American Oil Chemists' Society, Champaign, Illinois. Deodorized commercial canola oil obtained from Canada Packers Inc., Toronto, Ontario was re-bleached before hydrogenation.

Hydrogenations were carried out in a 300-ml stainless steel Parr reactor. In a typical run, 157.5 ml canola oil was charged into the reactor with 1.65 g of methyl benzoate-$Cr(CO)_3$ and 1.26 g of commercial nickel catalyst (2 g of metal/l of oil). In other experiments the amount of methyl benzoate-chrome carbonyl was varied between 0.12 and 2.00 g chromium/l of oil. The mixture was heated to the selected temperature with stirring under a nitrogen atmosphere. Hydrogen was introduced into the system and the nitrogen displaced through the vent. The hydrogen pressure was then increased to 3.4 MPa. Oil samples were obtained through the sampling valve at regular intervals. The hydrogenations were performed at 175 C, 3.4 mPa and 565 rpm. The hydrogenated canola oil samples were filtered to remove suspended nickel from the product. Although some of the decomposed chrome carbonyl complex was retained in the mixture, it did not interfere with the following analyses.

Iodine values (IV) were determined by AOCS Wijs method Cd 1-25 (27). The total isolated *trans*-isomer content was determined by infrared spectrophotometry according to AOCS method Cd 14-61 (27), using a Beckman model IR-9 infrared spectrophotometer. The methyl esters of the hydrogenated oil samples were analyzed for fatty acid composition by gas chromatography using a Hewlett-Packard model 5840 instrument equipped with a flame ionization detector, and a 30 m glass column coated with SP-2330 and operated isothermally at 185 C. *Cis,cis*-methylene-interrupted fatty acids (CCMI) were determined enzymatically using lipoxidase by AOCS method Cd 15-78 (27).

Activity is expressed as the change in iodine value per minute, and the specific isomerization index (SII) is defined as the increase in *trans* concentration per unit reduction of iodine value multiplied by 100. From the fatty acid composition of the initial and hydrogenated canola oils, linoleate and linolenate selectivities were determined using the conventional technique of Albright (28) and Allen (29) assuming that reactions proceed consecutively:

$$\text{Trienes} \xrightarrow{k_1} \text{Dienes} \xrightarrow{k_2} \text{Monoenes} \xrightarrow{k_3} \text{Saturates}$$

In calculating the selectivities based on this mechanism, it is assumed that all the isomers of individual fatty acids have the same rate of reaction. Linolenate (S_{Ln}) and linoleate (S_{Lo}) selectivities are expressed as $S_{Ln} = k_1/k_2$ and $S_{Lo} = k_2/k_3$, respectively, where k_1, k_2 and k_3 are the rate constants for the transformation of linolenic to linoleic, linoleic to oleic and oleic to stearic acid, respectively.

Four replicates for each run were performed and

TABLE 1

Hydrogenation of Canola Oil by Methyl Benzoate-$Cr(CO)_3$, Nickel and Mixed Catalysts[a]

	None	A	B	C	D	E	F	G	H
Catalysts									
(metal g/l) Ni		2.00	2.00	2.00	2.00	2.00	2.00	2.00	0.0
(metal g/l) Cr		0.00	2.00	0.48	0.25	0.22	0.19	0.12	2.00
(molar ratio) Ni/Cr		—	0.89	3.73	7.19	8.12	9.35	14.38	0.0
Analysis %									
Palmitate	4.1	3.4	3.4	3.3	3.5	3.7	3.8	3.4	4.4
Stearate	1.4	75.4	2.1	3.4	5.9	20.6	48.6	50.5	1.5
Monoenes	60.0	19.3	71.1	66.6	72.6	61.9	45.6	44.0	76.7
Dienes	22.7	0.0	17.9	20.0	14.4	11.1	0.5	0.2	14.0
Trienes	10.5	0.0	3.6	4.7	1.8	1.1	0.1	0.0	2.5
IV Wijs[b]	117.6	20.4	104.1	105.4	95.1	81.1	43.3	41.9	100.4
Trans[b] %	0.0	10.7	2.6	6.5	12.8	18.6	18.0	17.4	3.1
Linolenate selectivity S_{Ln}[c]		—	1.89	2.05	1.98	1.86	0.92	—	1.50
Linoleate selectivity S_{Lo}[c]		—	62.56	13.11	13.56	3.93	6.66	—	—
Specific isomerization index (SII)		11.0	19.31	53.32	56.89	51.07	24.23	23.04	18.02
Activity		3.24	0.45	0.41	0.75	1.22	2.48	2.52	0.57

[a] Temperature 175 C, agitation 565 rpm, pressure 3.4 MPa, time 30 min.

[b] No significant difference (P = 0.01) within iodine values and % *trans* content was obtained in several repetitions of individual experiments.

[c] Linolenate and linoleate selectivities calculated by AOCS Method Tz 16-79.

subjected to analysis of variance (30).

RESULTS AND DISCUSSION

Canola oil was hydrogenated in the presence of nickel, the homogeneous methyl benzoate-chromium tricarbonyl complex, and a mixture of these two catalysts.

Table 1 gives the results obtained for these hydrogenation runs. The fatty acid analyses do not give values for 20:0, 22:0, 22:1 accounting from the slight deviation from 100%.

It has been shown previously that there is a distinct difference in activity and selectivity between nickel and methyl benzoate-$Cr(CO)_3$. Nickel catalyst has the advantage of being very active compared to the chromium complex. However, it has high SII values and low linoleate selectivity (23).

When equal amounts of both catalysts were used during hydrogenation, the change in iodine value, *trans*-isomer content and product composition were almost identical to those produced by the methyl benzoate-$Cr(CO)_3$ complex alone. It seemed as if the chromium tricarbonyl complex completely blanked off all the active sites on the nickel catalyst, eliminating its catalytic activity. Only when the chromium tricarbonyl complex was reduced to about a tenth of the original concentration, while keeping the nickel concentration constant, did the characteristic behavior of the nickel catalyst begin to emerge. When the chromium concentration fell below 0.25 g/l the activity of the mixed-catalyst system increased drastically with a very small change in chromium concentrations (catalyst D and E), and the system began to approach the behavior of pure nickel (Table 1). In a recent paper (23) we have shown that methyl benzoate-$Cr(CO)_3$ gives an oil composed mostly of 18:1 monoenes and 18:2 dienes. The composition of canola oil obtained after 30 min of hydrogenation with the chrome carbonyl complex alone is given in Table 1 as 76.7% monoenes, 14.0% dienes and 2.5% trienes. The *trans*-isomer content was 3.1% at an iodine value of 100.4. With the mixed-catalyst system (catalysts B, C, D, E, F and G) we obtained oils which contained 4.7-0% trienes, 20.0-0.2% dienes, 72.6-44.0% monoenes and 50.5-2.1% stearate after 30 min of hydrogenation (Table 1).

Iodine values and levels of *trans*-isomers during hydrogenation of canola oil with mixtures of nickel catalyst and methyl benzoate-$Cr(CO)_3$ are presented in Figures 1 and 2. From the data it can be derived that at an iodine value of 100 a *trans*-acid content of 19.5, 1.8, 10.8, 13.0 and 3.4 was produced with catalysts A, B, D, E and H, respectively. Catalyst A (nickel only) gave rise to the lowest iodine value of these eight catalyst systems, while catalysts B, C and H gave the highest iodine values. As the Cr content fell from 0.25 g/l to zero, iodine values ranged from 95.1 to 20.4 (Table 1).

With nickel catalyst alone (catalyst A), *trans* fatty acids, after reaching a maximum level (25%), declined rapidly as the *trans*-isomers were saturated on further hydrogenation (Fig. 2). Catalysts B and H initially gave rise to a small increase in *trans*-acid concentration which leveled off during the rest of the run. Catalyst E began to approach the behavior of pure nickel (Catalyst A).

Figures 3-8 illustrate the variations in the levels of C_{18} fatty acids which in total account for 94-96% of the fatty acids in canola oil. Hydrogenation with catalyst A (nickel) resulted in a rapid hydrogenation of linoleic and oleic acids to produce oils containing mostly stearate. A different pattern was observed with catalyst H, which produces mainly oleic acid-containing oils (23).

The linolenate and linoleate selectivities were deter-

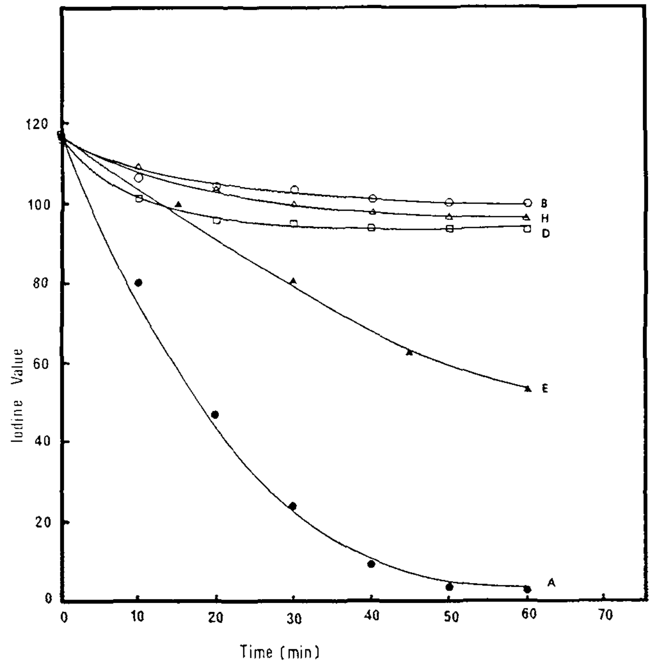

FIG. 1. **Variation of iodine values with time. Catalysts: ●, A; ○, B; □,D; ▲, E; △, H. (For composition of catalyst systems see Table 1.)**

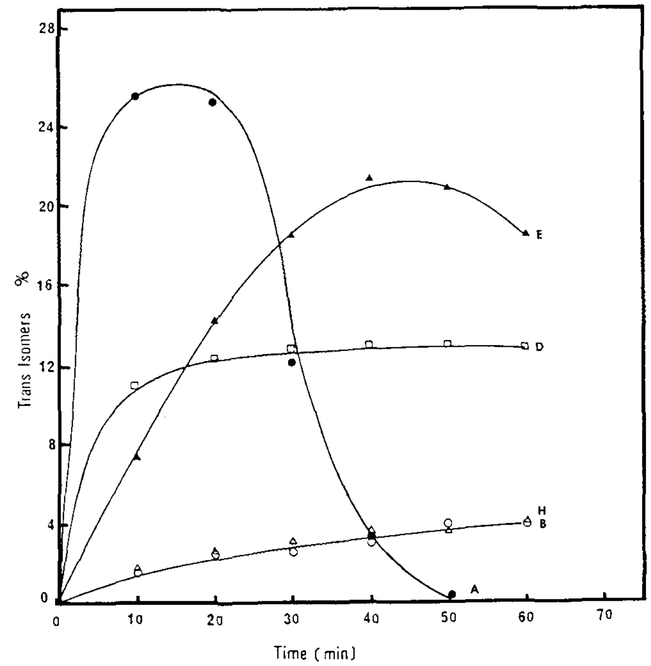

FIG. 2. ***Trans* fatty acids as a function of time. Catalysts: ●, A; ○, B; □, D; ▲, E; △, H. (For composition of catalyst systems see Table 1.)**

mined for each catalyst combination and listed in Tables 1 and 2. Linolenate selectivities of catalysts B, D and H obtained after 60 min of hydrogenation were 1.81, 2.13 and 1.96, respectively (Table 2). With catalyst A the hydrogenation rapidly reduced the concentration of trienes and dienes, which made it impossible to calculate linolenate and linoleate selectivities except for 10-min samples.

Table 1 shows that the linoleate selectivity of catalyst H was extremely high, whereas catalyst B showed higher linoleate selectivity than catalyst D. The extremely high linoleate selectivity of catalyst H resulted in a negligible increase in stearate content and a significant increase (27.8%) in the monoene content of the product.

The highest activity was observed with catalyst A and the lowest activities with catalysts H, B and C. However, further reduction in chromium content caused

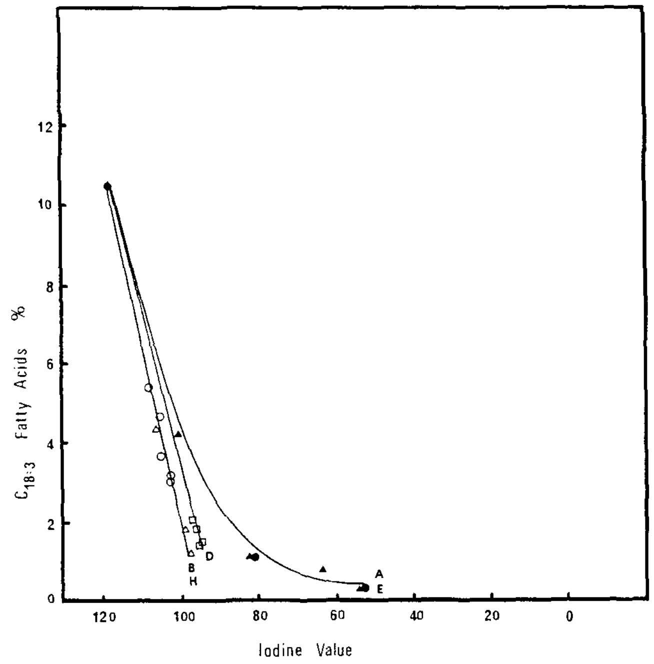

FIG. 3. 18:3 Fatty acids as a function of iodine value. Catalysts: ●, A; ○, B; □, D; ▲, E; △, H. (For composition of catalyst systems see Table 1.)

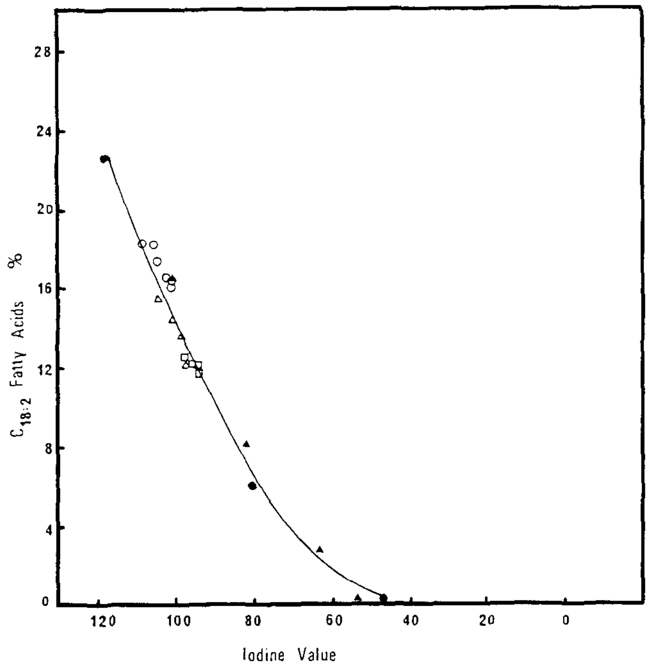

FIG. 4. 18:2 Fatty acids as a function of iodine value. Catalysts: ●, A; ○, B; □, D; ▲, E; △, H. (For composition of catalyst systems see Table 1.)

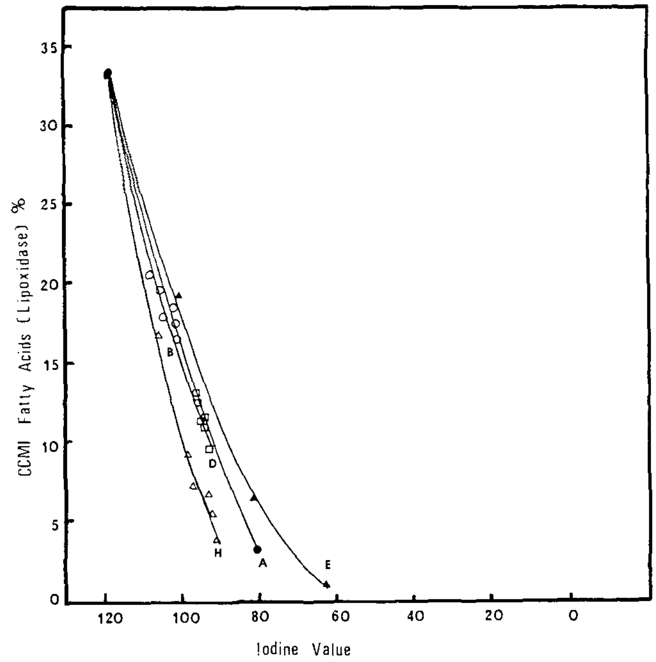

FIG. 5. *Cis,cis*-methylene-interrupted (CCMI) fatty acids as a function of iodine value. Catalysts: ●, A; ○, B; □, D; ▲, E; △, H. (For composition of catalyst systems see Table 1.)

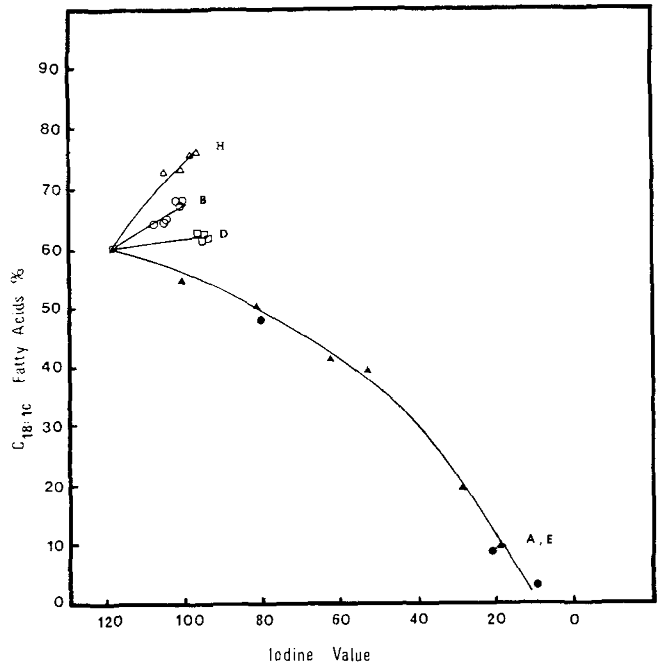

FIG. 6. 18:1c Fatty acids as a function of iodine value. Catalysts: ●, A; ○, B; □, D; ▲, E; △, H. (For composition of catalyst systems see Table 1.)

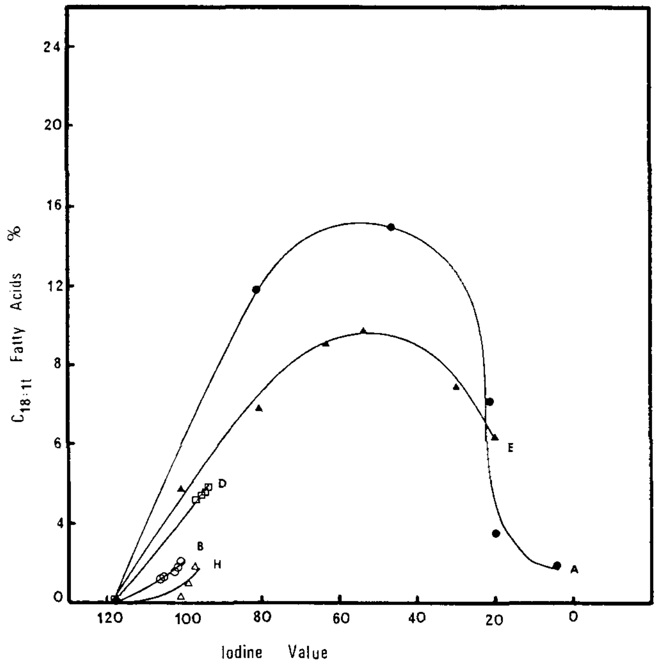

FIG. 7. 18:1t Fatty acids as a function of iodine value. Catalysts: ●, A; ○, B; □, D; ▲, E; △, H. (For composition of catalyst systems see Table 1.)

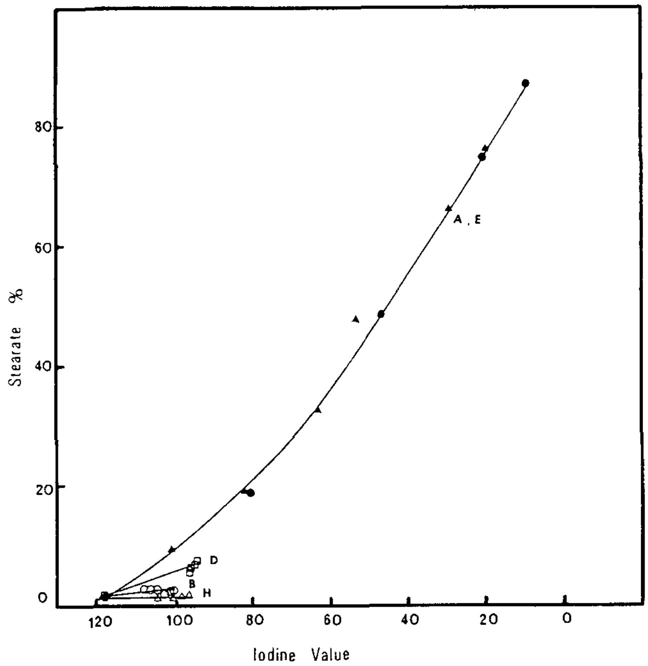

FIG. 8. Stearic acid as a function of iodine value. Catalysts: ●, A; ○, B; □, D; ▲, E; △, H. (For composition of catalyst systems see Table 1.)

a significant increase in activity changing from 0.41 for catalyst C to 2.52 for catalyst G (Table 1).

Catalyst B (2 g/l of each of methyl benzoate-$Cr(CO)_3$ and Ni) gives about the same SII values as chromium alone (catalyst H). However, when the chromium is reduced the increase in *trans* is reflected in the SII values (Table 1).

Maximum SII values were observed using nickel (catalyst A) alone (Table 2). The high SII value of 67.91 observed during the first 10 min of the run fell to zero with the progress of hydrogenation as the oil approached saturation. In contrast, the chrome-carbonyl hydrogenation of canola oils resulted in fairly constant specific isomerization index values, starting with 21.43 at an iodine value of 109.2. It reached a low of 17.86 at an iodine value of 98, increasing to 19.33 at an iodine value of 96.4, indicating a high *cis* selectivity. The mixed-catalyst system (catalyst B) produced a slightly lower SII value, 15.53, than that produced by methyl benzoate-$Cr(CO)_3$ (catalyst H). On further hydrogenation, SII values increased to 23.39 for catalyst B at an IV of 100.9, corresponding to 18.02 obtained for catalyst H. SII values increased as the chromium content of the catalyst fell to 0.25 g/l (Table 2, Catalyst D). The initial SII values given by catalyst D were close to those obtained with catalyst A. However, in contrast to catalyst A (Table 2), further reductions in SII values were not observed. Catalyst D thus has a unique character which is like neither Ni nor Cr. It contains, to some extent, the better characteristics of both: relatively low *trans*-isomer production, and an activity closer to that of Ni than catalysts B or H.

Chromium-tricarbonyl catalyzed hydrogenation yields a product distribution which is low in trienes and saturates and high in monoenes, with substantial quantities of the nutritionally important linoleic acid remaining. The advantage of the excellent selectivity of this complex toward *cis*-isomer formation is offset by the disadvantage of its low activity compared to that of the nickel catalyst. Its price is another drawback; it is much more expensive than the commercial nickel catalyst. We have found that the combination of about 10% chromium with nickel (catalyst D) gives an oil similar in composition to that given by the chromium complex alone, except for *trans* content. Without Ni the chromium catalyst at the level used in the case of catalyst D would be completely inactive (Fig. 9). The *trans* content of the oil thus produced is 3.5 times higher than that obtained with chromium alone at IV 100; however, it is only one-half of that given by Ni under the same conditions.

Figures 3-8 show the percentage of 18:3, 18:2, CCMI dienes, 18:1c, 18:1t and 18:0 fatty acids as a function of iodine value for catalysts A, B, D, E and H. The reduction of 18:3 fatty acids was similar (within 2.5 percentage points) for all the catalysts at an iodine value of 100 (Fig. 3). Below this level only catalysts A and E were active enough to cause a further reduction in trienes. However, the considerable drop in reactivity after 100 IV may be due to the difference in the reactivities of the geometrical and positional isomers formed during the hydrogenation (23). For catalysts B and D the reaction did not continue further and showed the characteristic behavior of chromium alone (catalyst H). For 18:2 fatty acids the same overall reactivity for each catalyst was obtained (Fig. 4). In the latter part of the hydrogenation (below 90 IV) the Ni-dominated reactions continued further to hydrogenate geometrical and positional isomers, whereas the chrome carbonyl complex showed no activity.

TABLE 2

Hydrogenation of Canola Oil in the Presence of Methyl Benzoate-$Cr(CO)_3$, Nickel and Mixed Catalysts[a]

Mixed catalyst systems	Hydrogenatin time (min)	IV	% *trans*	SII	Activity	Linolenate selectivity (S_{Ln})	Linoleate selectivity (S_{Lo})
A (Ni only)	10	79.9	25.6	67.91	3.77	1.49	5.39
	20	46.5	25.3	35.58	3.56	—	—
	30	20.4	10.7	11.00	3.24	—	—
	40	9.0	3.4	3.13	2.73	—	—
	50	3.6	0.3	0.26	2.28	—	—
	60	2.7	0.0	0.0	1.92	—	—
B (Ni/Cr = 0.89)	10	107.3	1.6	15.53	1.03	1.57	34.26
	20	104.8	2.5	19.53	0.64	1.75	43.83
	30	104.1	2.6	19.26	0.45	1.89	62.56
	40	101.5	3.1	19.25	0.40	1.89	53.97
	50	100.8	4.0	23.81	0.34	1.81	56.51
	60	100.5	4.0	23.39	0.29	1.81	64.67
D (Ni/Cr = 7.19)	10	101.3	11.0	67.48	1.63	1.87	15.52
	20	96.0	12.4	57.41	1.08	1.96	14.53
	30	95.1	12.8	56.89	0.75	1.98	13.56
	40	94.0	13.0	55.08	0.59	2.14	12.65
	50	93.8	13.0	54.62	0.48	2.24	11.71
	60	93.6	12.8	53.33	0.40	2.13	10.69
H (Cr only)	10	109.2	1.8	21.43	0.84	1.16	—
	20	104.3	2.6	19.55	0.67	1.33	—
	30	100.4	3.1	18.02	0.57	1.50	—
	40	98.0	3.5	17.86	0.49	1.68	—
	50	97.2	3.8	18.62	0.41	1.84	—
	60	96.4	4.1	19.33	0.35	1.96	—

[a] Catalyst concentrations are given as g metal/l oil. A, 2 g/l Ni; B, 2 g/l Ni and 2 g/l Cr; D, 2 g/l Ni and 0.25 g/l Cr; H, 2 g/l Cr.

The concentration of CCMI fatty acids as determined by the lipoxidase method, versus iodine values, is given in Figure 5. The chrome carbonyl-catalyzed reduction is faster than that of nickel. It is well known that the two catalysts, nickel and chrome carbonyl, catalyze the hydrogenation reaction through different mechanisms (31,32). The methylene-interrupted dienes are expected to react faster than the dienes separated by two or more methylene groups, since conjugation is the rate-determining step for the chrome-catalyzed reactions (23,32).

Figures 6 and 7 illustrate the concentrations of 18:1c and 18:1t fatty acids as a function of iodine value. There is a distinct difference between catalyst A and H. Figure 6 shows the high *cis* selectivity of catalyst H (Cr only) compared to A (Ni only), and also illustrates the advantage of adding small amounts of chrome carbonyl to nickel, thus greatly influencing its *cis* selectivity. As the chrome-carbonyl content of the mixture was reduced, an increase in 18:1t and a decrease in 18:1c was observed. Figures 6 and 7 show the advantage of the mixed catalyst D which has a higher selectivity toward *cis* production than the nickel but has an activity which is 50% higher than that of the chromium complex, catalyst H (Table 1). A further advantage of catalyst D is illustrated in Figure 8. It gives a much lower stearate content than catalyst A. It is clear that these changes

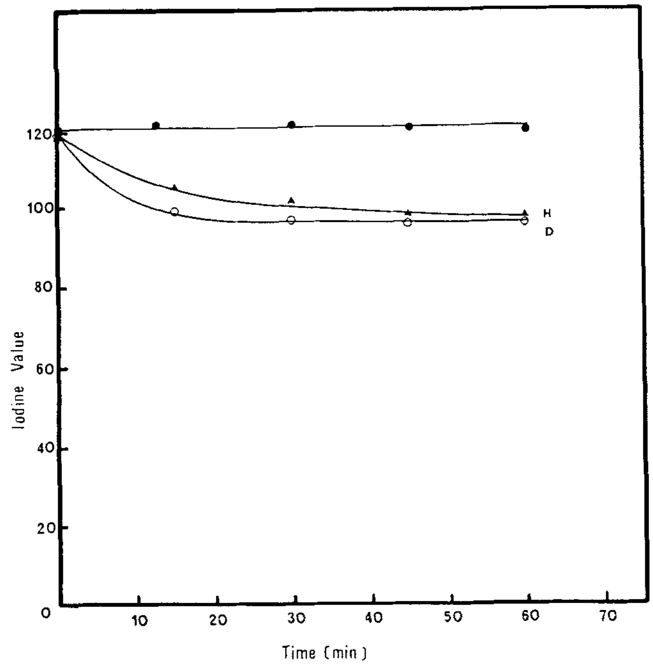

FIG. 9. Iodine values as a function of time. ●, 0.25 g/l Cr; ○, 2 g/l Ni, 0.25 g/l Cr (catalyst D); ▲, 2 g/l Cr (catalyst H).

are not caused by chrome carbonyl alone, because chrome carbonyl has no catalytic activity at such low concentration in the absence of nickel (Figure 9).

In the transition zone where the chrome carbonyl content was about 0.25 g/l (e.g. catalysts D and E), the *trans*-isomer content was lower than that for nickel alone at IV 100. By changing the temperature and pressure one may be able to obtain low *trans*-isomer formation and low iodine values with a reasonable activity.

It is apparent from these results that the molar ratio of Ni/Cr of 7 (catalyst D) has some theoretical importance. Above this ratio, the mixed catalyst behaves like nickel; below, it behaves like chrome carbonyl. One can only speculate as to how the two catalysts actually interact with each other. Do they bind to each other and, if so, by what mechanism? How much methyl benzoate-$Cr(CO)_3$ is needed to inactivate one active site on the nickel catalyst? Perhaps one could thus determine the number of active sites on nickel, which would be very useful for catalyst characterization. Also, this may be applicable to other catalysts.

Further work is required before this or other mixed-catalyst systems could be used in edible-oil hydrogenation. Mixed-catalyst systems may offer a method of producing an immobilized methyl benzoate-$Cr(CO)_3$ catalyst that will permit the removal of the chromium complex by filtration after the completion of the hydrogenation reaction.

More generally, we may be able to combine homogeneous with heterogeneous catalysts while retaining the advantages of both. This could bring us one step closer to producing custom-designed catalyst systems for industrial use.

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